

# An anion exchange resin from soybean hulls<sup>†</sup>

Wayne E Marshall\* and Lynda H Wartelle

USDA-ARS, Southern Regional Research Center, 1100 Robert E Lee Blvd, PO Box 19687, New Orleans, LA 70179-0687, USA

**Abstract:** Agricultural by-products are generally poor adsorbents of anions in solution. Therefore, modification of the by-product could enhance its anion exchange capabilities. The objective of this study was to increase the anion exchange properties of the agricultural by-product, soybean hulls, by chemical modification. Soybean hulls were quaternized with the quaternizing agent, *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, in the presence of a strongly alkaline environment. This modification increased the amount of positive charge on the hulls as evidenced by increased nitrogen content and increased uptake of anions compared with the unmodified hulls. A method to optimize the anion exchange properties of the hulls was developed. Ion exchange properties of the hulls toward anions of environmental significance, namely arsenate (As), chromate (Cr), dichromate (Cr<sub>2</sub>), phosphate (P) and selenate (Se) were determined. The modified hulls were also compared with commercial cellulose-based and synthetic anion exchange resins in their ability to remove these anions from solution. The experimental and commercial resins were also compared for their ability to remove a mixture of arsenate, chromate, dichromate and selenate from laboratory prepared solutions to levels below the maximum contaminant levels for these anions in drinking water as specified by the US Environmental Protection Agency (US EPA). Our results demonstrate that the soy hull resin is more efficient in anion removal than the commercial cellulose-based resin but not as effective as the commercial synthetic resin.

Published in 2004 for SCI by John Wiley & Sons, Ltd.

**Keywords:** soybean hulls; anion adsorption; anion exchange resin; quaternization; *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride

## 1 INTRODUCTION

A number of serious environmental concerns have arisen over the last few years that could be helped by the application of anion exchange resins. These include phosphate remediation of groundwater in the Midwestern US, the removal of arsenic from potable water wells in the Southwestern US, and the reduction of selenium in irrigation water in California's Central Valley. Since these projects could use potentially massive amounts of resin, anion exchangers made from renewable resources produced in large quantity may be required. Such renewable materials are agricultural by-products. Readily available agricultural by-products such as soybean hulls have high cellulose content,<sup>1</sup> while others, such as pecan shells, have a lower cellulose, but high lignin, content.<sup>1</sup> The quaternization of lignocellulosic materials to produce anion exchange resins has the potential to fill a need for inexpensive, effective removal of anions from wastewater.

The quaternization of natural polymers such as cellulose<sup>2,3</sup> and lignocellulose<sup>4–6</sup> found in plant-derived agricultural by-products and the actual by-products themselves<sup>7–16</sup> has been investigated by the reaction of these polymers with a number of quaternary

ammonium compounds. These compounds primarily combine with alcoholic –OH groups in cellulose and with phenolic –OH groups in the lignin moieties of these by-products. Most of these reactions are accomplished by cross-linking the material with various cross-linking agents, then quaternizing them with various *N*-substituted amines.

Youssef<sup>2</sup> developed quaternized cellulose derivatives and used them for the adsorption of acid dyes. A decrease in adsorption due to an increase in pH was observed for the modified cellulose. Navarro *et al*<sup>3</sup> synthesized an adsorbent for heavy metals by reacting cellulose with epichlorohydrin and polyethyleneimine and obtained a product with an adsorption capacity of 1.44 mmol g<sup>–1</sup> for mercury. Antal *et al*<sup>4,5</sup> described the preparation and distribution of functional groups in lignocellulosic material after reaction with *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride. The effect of the reaction was found to be limited to the cell wall surface using beech sawdust as the source of lignocellulose. Since lignin created a network across the cell wall surface, the reaction between *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride and cellulose was hindered. Ebringerova *et al*<sup>6</sup>

\* Correspondence to: Wayne E Marshall, USDA-ARS, Southern Regional Research Center, 1100 Robert E Lee Blvd, PO Box 19687, New Orleans, LA 70179-0687, USA  
E-mail: marshall@srrc.ars.usda.gov

<sup>†</sup>This article is a US Government work and is in the public domain in the USA.

(Received 11 May 2004; revised version received 21 June 2004; accepted 22 June 2004)

Published online 7 September 2004

indicated that lignin also influences the distribution of functional groups after reaction with *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, but does not influence the reactivity of hemicellulose, unlike cellulose.

*N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride is a very versatile reagent. It has been used to modify a number of diverse agricultural by-products, including aspen wood meal,<sup>7</sup> spruce wood meal,<sup>8</sup> sugarcane bagasse,<sup>9,11</sup> corn cob meal,<sup>10</sup> pea stem polysaccharides,<sup>12</sup> and beech sawdust and wheat straw.<sup>14</sup>

In addition to *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, other quaternizing systems have been used to create agricultural by-products with anion exchange capacity. Baes *et al*<sup>13</sup> reacted coconut coir with methylamine in a basic medium to form a product with adsorption capacities for arsenic, chromium, nitrates and selenium anions at 0.086, 0.327, 0.459, and 0.222 mmol g<sup>-1</sup>, respectively. Orlando *et al*<sup>15,16</sup> reacted several by-products including sugarcane bagasse and rice hulls by cross-linking with epichlorohydrin and reacting with dimethylamine in dimethylformamide using pyridine as an accelerant to form an effective anion exchanger for nitrate ion. The authors reported nitrate exchange capacities of 1.41 mmol g<sup>-1</sup> for sugarcane bagasse and 1.32 mmol g<sup>-1</sup> for rice hulls.

Based on the above references, anion exchange resins can be created from agricultural by-products that have affinities toward different anions of environmental concern. The objectives of this study were to determine optimum reaction conditions for the production of an anion exchange resin from a high volume, low cost, lignocellulosic by-product, namely soybean hulls, and compare the resulting anion exchange material for removal of various anions of environmental concern to two commercial anion exchange resins, one a polystyrene-divinylbenzene-based resin, and the other a cellulose-based resin.

## 2 MATERIALS AND METHODS

### 2.1 Materials

Reagent grade chemicals used as adsorbates were sodium monohydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>), sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), potassium chromate (K<sub>2</sub>CrO<sub>4</sub>), sodium arsenate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O) and sodium selenate (Na<sub>2</sub>SeO<sub>4</sub>) and were purchased from Sigma Chemical Co (St Louis, MO) or Fisher Scientific (Pittsburgh, PA). Soybean hulls were obtained from Owensboro Grain Co (Owensboro, KY). Quat 188 [65% solution of *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride] was a gift from the Dow Chemical Co (Freeport, TX). A commercially available, quaternary ammonium cellulose anion exchange resin (QA 52) was procured from Whatman International, Ltd (Maidstone, England) and a polystyrene-divinylbenzene-based, strong anion

exchange resin (Amberlite IRA-400), with quaternary ammonium groups as the cationic binding sites, was purchased from Supelco (Bellefonte, PA).

### 2.2 Optimization of reaction conditions for quaternization

Soybean hulls (0.85–2.00 mm particle size) were base washed by stirring 50 g of hulls in a 1.0 dm<sup>3</sup> solution of 1% (w/v) Na<sub>2</sub>CO<sub>3</sub> and 1% (w/v) NaCl for 2 h according to the method of Laszlo.<sup>11</sup> The material was rinsed with deionized water and dried at 60 °C.

Samples (3 g) of base-washed soy hulls were incubated with different concentrations of NaOH for 30 min and at 25 °C. *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride was then added in different amounts to each sample to produce different NaOH:*N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride ratios.

Samples were reacted in either a forced air oven or a vacuum oven at different temperatures for various incubation times. The reacted products were suspended in 1.5 dm<sup>3</sup> of deionized water and converted to the chloride form by adjusting their pH to 2 with 5 mol dm<sup>-3</sup> HCl. The products were then filtered and washed with 500 cm<sup>3</sup> deionized water and dried at 60 °C to a moisture content of less than 10%.

The amount of nitrogen (N) added to the soybean hulls from the quaternization reaction are given by:

$$N \text{ added (mmol N g}^{-1}\text{)} = [(\%N_{\text{quat}} - \%N_{\text{bw}}) \times 0.714] \quad (1)$$

where %*N*<sub>quat</sub> = percent nitrogen in the quaternized sample and %*N*<sub>bw</sub> = percent nitrogen in the base-washed sample. The factor 0.714 converts %N to mmol N g<sup>-1</sup> of soybean hulls.

Reaction efficiency for addition of a quaternary amine to soybean hulls for the optimized quaternization process was determined by the equation:

$$\text{Reaction efficiency (\%)} = \{[N \text{ added (mmol N g}^{-1}\text{)}] / 20.0\} \times 100 \quad (2)$$

where the factor 20.0 = mmol of *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride added to the reaction mixture per gram of soybean hulls.

Percent nitrogen was determined by a Leco model FP-428 nitrogen analyzer (St Joseph, MI) according to the manufacturer's instructions.

Product yield was calculated by the equation:

$$\text{Product yield (\%)} = (W_{\text{gt}_{\text{quat}}} / W_{\text{gt}_{\text{bw}}}) \times 100 \quad (3)$$

where *W*<sub>gt<sub>quat</sub></sub> = dry weight of quaternized sample and *W*<sub>gt<sub>bw</sub></sub> = dry weight of base-washed sample.

### 2.3 Determination of phosphorus and other anion adsorption

To determine optimum reaction conditions for quaternization, a phosphorus adsorption assay was

conducted in batch mode using 0.5 g quaternized soybean hull samples in 50 cm<sup>3</sup> of 20 mmol dm<sup>-3</sup> phosphorus solution prepared from Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>, buffered at pH 7. The solutions were stirred for 24 h at 25 °C and 300 rpm, then filtered with a 0.22 µm filter and diluted in 4% HNO<sub>3</sub>. Phosphorus concentrations were determined axially at 213.618 nm by Inductively Coupled Plasma-Atomic Emission Spectrometry on an instrument (Leeman Labs Profile) with dual view capabilities (Leeman Labs, Hudson, NH).

To determine the adsorption characteristics of quaternized soybean hulls, adsorption efficiencies and adsorption isotherms toward five different anions [arsenate (As), chromate (Cr), dichromate (Cr<sub>2</sub>), phosphate (P) and selenate (Se)] were evaluated. The adsorption assay described above was used to determine only phosphate adsorption from solution. For the other four anions, no phosphate buffer was used. The pH of the assay solutions was kept at 7 by adjustment with either 0.1 mol dm<sup>-3</sup> NaOH or 0.1 mol dm<sup>-3</sup> HCl.

For adsorption capacity studies and for the construction of adsorption isotherms, concentrations of the five anions, as As, Cr, Cr<sub>2</sub>, P and Se, ranged from 0 mmol dm<sup>-3</sup> to 20 mmol dm<sup>-3</sup> and saturation of the resin was achieved for all anions at about 10 mmol dm<sup>-3</sup> concentrations. Concentrations of As, Cr and Se were determined with the ICP-AES in axial mode at wavelengths of 193.695 nm, 267.716 nm, and 196.026 nm, respectively.

The isotherms were evaluated using the non-linear Langmuir model<sup>17</sup> for adsorbent-adsorbate interaction, as given by the following equation:

$$q_e = KC_e Q_o / (1 + KC_e) \quad (4)$$

where  $C_e$  is the equilibrium anion concentration in solution,  $q_e$  is the amount of anion adsorbed per unit mass,  $Q_o$  is the adsorption maximum and  $K$  is the affinity or association constant of anion for adsorbent. Langmuir parameters for adsorption capacity and association constant were determined by a non-linear regression analysis of the adsorption isotherms using Sigma Plot, v 7 (SPSS, Chicago, IL). This program also determines the correlation coefficient ( $r^2$ ) and the 'goodness of fit' parameter ( $p$ ) for each adsorption isotherm.

## 2.4 Determination of competitive anion adsorption

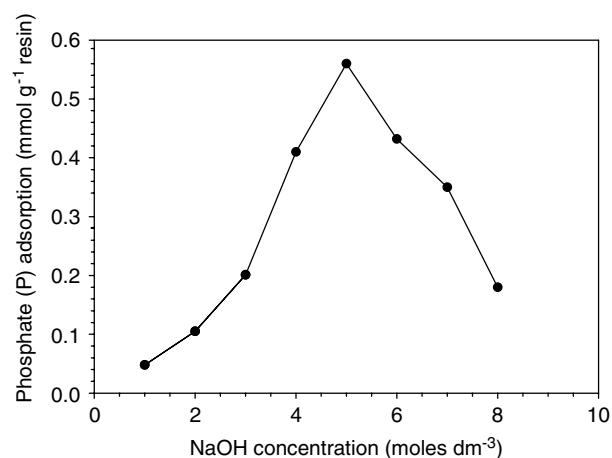
Competitive adsorption studies were carried out at pH 7.0 and 25 °C for 24 h with stirring at 300 rpm using 0.5 g of quaternized soybean hulls or 0.5 g of either of two commercial anion exchange resins, Whatman QA 52 or Supelco IRA-400, in 50 cm<sup>3</sup> of solution. Solution concentrations were prepared to be 10 or 50 times above the US EPA drinking water limits for As (0.050 ppm), total Cr (0.100 ppm) and Se (0.050 ppm).<sup>18</sup> There are no published US

EPA drinking water limits for P, so it was not included in the solution. Solutions containing As, Cr and Se at 50 times the US EPA limit were also prepared in the presence of a simulated hard water environment. Simulated hard water contained 40 ppm CaCl<sub>2</sub> (100 ppm calcium carbonate equivalent) and 3.33 ppm MgCl<sub>2</sub> (10 ppm magnesium carbonate equivalent), in addition to the anions of interest. After incubation, the solutions were filtered, diluted with acid and analyzed as described above.

## 3 RESULTS AND DISCUSSION

### 3.1 Quaternized soybean hulls

In order to optimize reaction conditions for the quaternization of soybean hulls, the method of Laszlo<sup>11</sup> was used as a starting point. The concentration of NaOH used to treat the hulls before the addition of *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride was varied from 1 mol dm<sup>-3</sup> to 8 mol dm<sup>-3</sup> (Fig 1). Greatest P adsorption was seen at 5 mol dm<sup>-3</sup> NaOH (25 mmol NaOH g<sup>-1</sup> soybean hulls) with a considerable reduction in P uptake at either lower or higher concentrations of base (Fig 1). Using 5 mol dm<sup>-3</sup> NaOH, the amount of *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride was varied and the effect on P adsorption was monitored (Fig 2). Clearly, the most favored ratio was one part base to one part *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride on a volume/volume basis. In the absence of quaternizing agent, non-quaternized hulls had very little tendency to adsorb phosphorus (Fig 2). Apparently, soybean hulls have little positive charge in which to adsorb P. The addition of *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride in NaOH solution produced significant P adsorption starting at a ratio of 1.0:0.4. The addition of higher amounts of quaternizing agent improved P adsorption, up to a ratio of 1.0:1.0

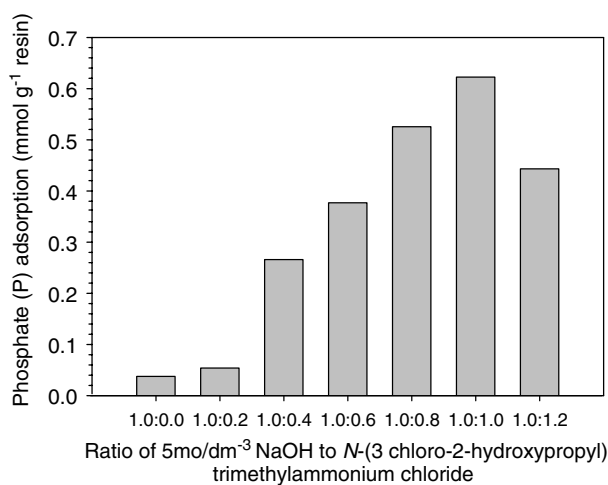


**Figure 1.** Phosphate (P) adsorption by quaternized soybean hulls prepared in the presence of different NaOH concentrations. Reaction conditions were 20 mmol g<sup>-1</sup> hulls of *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride with hulls incubated for 16 h at 80 °C. Each point represents the mean of duplicate samples where the SEM was <10% of the mean values.

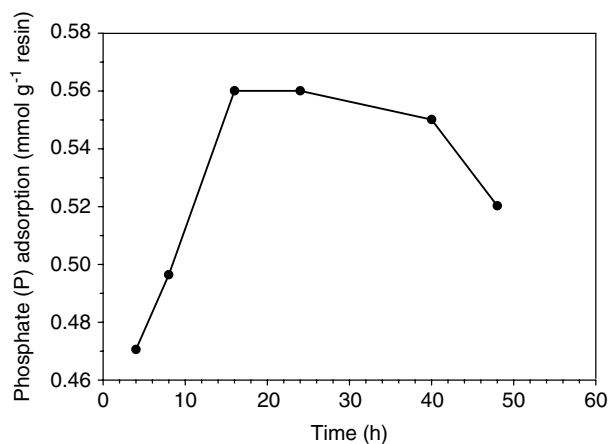
(25 mmol NaOH g<sup>-1</sup> hulls: 20 mmol *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride g<sup>-1</sup> hulls), where maximum P adsorption was observed. The addition of quaternizing agent beyond this concentration resulted in a product with lower P adsorption. The efficiency of the quaternizing reaction was reduced at higher levels of the reagent.

P adsorption increased sharply when the reaction time was increased from 2 h to 16 h, where maximum adsorption was observed (Fig 3). After 16 h, P adsorption slowly declined.

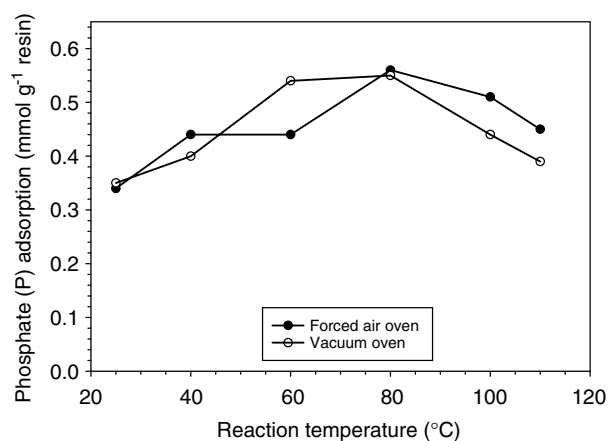
Optimum reaction temperature was evaluated by placing samples either in a forced air oven or a vacuum oven. The forced air oven appeared to dry the samples more quickly than the vacuum oven at a given temperature. Therefore, faster drying might affect the final product. Fig 4 shows that there was



**Figure 2.** Phosphate (P) adsorption by quaternized soybean hulls prepared in the presence of different ratios of NaOH to *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride. Reaction conditions were 25 mmol g<sup>-1</sup> hulls of NaOH with hulls incubated for 16 h at 80 °C. Each bar represents the mean of duplicate samples where the SEM was <10% of the mean values.



**Figure 3.** Phosphate (P) adsorption by quaternized soybean hulls prepared at different reaction times. Reaction conditions were 25 mmol g<sup>-1</sup> NaOH, 20 mmol g<sup>-1</sup> *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, with hulls incubated at 80 °C. Each point represents the mean of duplicate samples where the SEM was <10% of the mean values.



**Figure 4.** Phosphate (P) adsorption by quaternized soybean hulls prepared at different reaction temperatures. Reaction conditions were 25 mmol g<sup>-1</sup> NaOH, 20 mmol g<sup>-1</sup> *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, with hulls incubated for 16 h. Each point represents the mean of duplicate samples where the SEM was <10% of the mean values.

little difference in oven type on P adsorption. In both cases, optimum P adsorption was seen at 80 °C and was about 0.56 mmol P adsorbed g<sup>-1</sup> resin.

On the basis of the data depicted in Figs 1–4, an optimum method for quaternization of soybean hulls was established. Three g of soybean hulls were treated with 15 cm<sup>3</sup> of 5 mol dm<sup>-3</sup> NaOH (25 mmol NaOH g<sup>-1</sup> hulls) for 30 min in order to provide a basic environment for the quaternizing agent. Fifteen cm<sup>3</sup> of *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (20 mmol quat reagent g<sup>-1</sup> hulls) were added to the reaction mixture and the soybean hulls were incubated at 80 °C for 16 h. The pH adjustment, washing and drying steps were followed as described above under in Section 2.

The reaction between the hulls and the quaternizing agent was not particularly efficient. Based on the increase in N content (1.00%) after quaternization of the soybean hulls under optimized reaction conditions, 0.71 mmol of cationic groups were generated (based on eqn (1)) g<sup>-1</sup> hulls using 20.0 mmol of reagent g<sup>-1</sup> hulls. Thus, the efficiency of the reaction was 3.6% based on eqn (2). We assume that the amount of quaternizing agent was not limiting, so the accessibility of the reactive sites on the hulls would be the limiting factor.

Product yield of the quaternized by-product was 65% under optimum reaction conditions, based on eqn (3).

### 3.2 Anion adsorption by quaternized soybean hulls

Table 1 gives the adsorption capacities and association constants (Langmuir parameters) for the adsorption of five different anionic species to quaternized soybean hulls at pH 7. From the correlation coefficients (*r*<sup>2</sup>) and the 'goodness of fit' parameter (*p*), the Langmuir model adequately describes the adsorption isotherm

**Table 1.** Adsorption capacities and association constants for environmentally important anions, determined using soybean hull anion exchange resin as adsorbent<sup>a</sup>

Anion	Adsorption capacity (mmol g <sup>-1</sup> resin)	Association constant (dm <sup>3</sup> mmol <sup>-1</sup> )	<i>r</i> <sup>2</sup>	<i>p</i>
Arsenate (As)	0.52 ± 0.03	0.31 ± 0.14	0.90	<0.0001
Chromate (Cr)	0.68 ± 0.06	0.80 ± 0.34	0.91	<0.0001
Dichromate (Cr <sub>2</sub> )	0.65 ± 0.08	1.58 ± 0.61	0.96	<0.001
Phosphate (P)	0.63 ± 0.04	1.30 ± 0.44	0.94	<0.0001
Selenate (Se)	0.52 ± 0.05	0.14 ± 0.06	0.95	<0.001

<sup>a</sup> Adsorption capacities and association constants were obtained from adsorption isotherms using the Langmuir model in the non-linear form. The adsorption isotherms were generated at pH 7.

data. Thus, the Langmuir model appears to be valid for all data sets.

Adsorption capacities were relatively similar to each other and varied from 0.52 mmol g<sup>-1</sup> for As and Se to 0.68 mmol g<sup>-1</sup> for Cr as chromate. There appears to be roughly a 1:1 correspondence between adsorption capacity and the amount of N added to the soybean hulls after quaternization (0.71 mmol g<sup>-1</sup>). The small differences among adsorption capacities are probably inherent in the anions themselves, such as molecular size and degree of hydration.

The adsorption of the five anions as individual species by quaternized soybean hulls were compared with the adsorption of these anions by the two commercial resins (Table 2). A concentration of 20 mmol dm<sup>-3</sup> was used for each anion. This concentration was found to saturate the quaternized soybean hull binding sites and therefore represented a 'one-point' measurement of adsorption capacity. As a result, the 'one-point' values in Table 2 for modified soybean hulls were similar to the adsorption capacities measured from adsorption isotherms in Table 1. For all anions listed, quaternized soybean hulls adsorbed more of each anion than Whatman QA 52 but less of each anion than Amberlite IRA-400. The comparison between quaternized soybean hulls and Whatman QA 52 is particularly significant. Both resins contain a considerable percentage of cellulose, 67.6% for soybean hulls<sup>1</sup> and 100% for QA 52 (Whatman, product data sheet), so a direct comparison is reasonably valid. Additionally, we estimated that QA 52 had 1.07 mmol g<sup>-1</sup> cationic groups (Wartelle and Marshall, unpublished observations) compared with 0.71 mmol g<sup>-1</sup> cationic groups for soybean hulls. Amberlite IRA-400 is different from the other two

resins in that quaternary ammonium groups are attached to a backbone of styrene-divinylbenzene polymer and was estimated to contain 3.34 mmol g<sup>-1</sup> cationic groups (Wartelle and Marshall, unpublished observations). These values would explain the higher anion adsorption by Amberlite IRA-400 but would not explain the lower anion adsorption values for QA 52 compared with modified soybean hulls. Apparently modified soybean hulls provide more efficient binding than the cellulose-based resin at saturating conditions of the anions.

### 3.3 Competitive anion adsorption

Quaternized soybean hulls and the two commercial resins were compared for their efficacy in the removal of a mixture of As, total Cr and Se from laboratory-prepared solutions and from solutions that contained the hard water cations, calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) (Table 3). In these experiments, four anions (arsenate, chromate, dichromate, selenate) were present and the concentrations of these anions were approximately 10 or 50 times above the US EPA drinking water limits.<sup>18</sup>

At concentrations of approximately 10 times the US EPA drinking water limit, the resins removed As, total Cr and Se to below the detection limit of the ICP-AES spectrometer, which was 0.005 ppm for As and Cr, and 0.010 ppm for Se. Therefore, these anions were also removed to below the US EPA drinking water limits. When the concentrations of As, total Cr and Se were increased to approximately 50 times the US EPA drinking water limit, all resins were again successful in reducing the anion load to below the US EPA limit, although total Cr was detected in solutions treated with quaternized hulls and QA 52 and As was

**Table 2.** Adsorption of individual anions at 20 mmol dm<sup>-3</sup> concentrations by modified soybean hulls and two commercial anion exchange resins (Whatman QA 52, Amberlite IRA-400)

Ion exchange resin	Amount adsorbed <sup>a</sup> (mmol g <sup>-1</sup> dry wgt)				
	P (phosphate)	Cr <sub>2</sub> (dichromate)	Cr (chromate)	As (arsenate)	Se (selenate)
Modified soybean hulls	0.64 ± 0.01	0.56 ± 0.01	0.73 ± 0.02	0.48 ± 0.02	0.55 ± 0.07
Whatman QA 52	0.46 ± 0.01	0.43 ± 0.12	0.63 ± 0.01	0.36 ± 0.03	0.49 ± 0.01
Amberlite IRA-400	1.04 ± 0.00	1.07 ± 0.02	1.68 ± 0.02	0.90 ± 0.05	0.90 ± 0.38

<sup>a</sup> Mean ± SEM of duplicate determinations.

**Table 3.** The effect of anion concentration and water hardness on the ability of different anion exchange resins to remove select anions

Sample	Solution concentration (ppm) <sup>a</sup>		
	Total Cr <sup>b</sup>	As	Se
10× US EPA limit <sup>c</sup>			
Initial concentration	1.09	0.79	0.61
Quaternized soybean hulls	nd <sup>d</sup>	nd	nd
Whatman QA 52	nd	nd	nd
Amberlite IRA-400	nd	nd	nd
50× US EPA limit			
Initial concentration	5.63	2.75	2.67
Quaternized soybean hulls	0.08	0.03	nd
Whatman QA 52	0.01	nd	nd
Amberlite IRA-400	nd	nd	nd
50× US EPA limit with Ca and Mg ions added <sup>e</sup>			
Initial concentration	5.23	2.30	2.36
Quaternized soybean hulls	0.20	0.28	nd
Whatman QA 52	0.07	0.08	nd
Amberlite IRA-400	nd	0.01	nd

<sup>a</sup> Means of duplicate samples where the SEM was <10% of the mean values.

<sup>b</sup> Total chromium based on equal parts of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and CrO<sub>4</sub><sup>2-</sup> in each simulated wastewater solution.

<sup>c</sup> The US EPA drinking water limits for total chromium (Cr), arsenate (As) and selenate (Se) are 0.100 ppm, 0.050 ppm and 0.050 ppm, respectively.

<sup>d</sup> Not detected. Concentrations were below the detectable instrumentation limit of 0.005 ppm for total Cr, 0.005 ppm for As and 0.010 ppm for Se.

<sup>e</sup> The 50× hard water sample was created by adding 100 ppm CaCO<sub>3</sub> equivalent (as CaCl<sub>2</sub>) and 10 ppm MgCO<sub>3</sub> equivalent (as MgCl<sub>2</sub>) to the mixture of anions. This solution is classified as moderately hard water according to Renn.<sup>19</sup>

now detected in the solution treated with quaternized hulls (Table 3). The addition of hard water cations to a mixture of the anions resulted in more total Cr in solutions treated with both quaternized soybean hulls and Whatman QA 52 (Table 3) and more As in solutions treated with all of the resins. Concentrations of As were now above the US EPA drinking water limit in the samples containing quaternized soybean hulls and Whatman QA 52. Se was still effectively removed by all resins even in the presence of the hard water cations.

The adsorption of anions by quaternized soybean hulls was most affected by the introduction of calcium and magnesium ions to the anion solution. The reason for this observation was not readily apparent, especially since the binding of total Cr and As was affected but not the binding of Se. Apparently, the commercial resins can compete somewhat better than quaternized soybean hulls for the anions in the presence of the hard water cations.

#### 4 CONCLUSIONS

In this study, the agricultural by-product, soybean hulls, was modified with the quaternizing reagent,

*N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, to create an anion exchange resin. Under optimal reaction conditions of NaOH and *N*-(3-chloro-2-hydroxypropyl) trimethylammonium chloride concentrations, time and temperature, 0.71 mmol of trimethylammonium cation was incorporated g<sup>-1</sup> of hulls. This value places an upper limit on the amount of anion binding possible, which is reflected in the adsorption capacities of five different anions of environmental interest that varied from 0.52 to 0.68 mmol g<sup>-1</sup> of modified hulls. Also, in this study, quaternized soybean hulls were found to be more effective than a commercial, cellulose-based resin, QA 52, at select anion adsorption. This result may pave the way for further consideration of modified soybean hulls as a potentially useful anion exchange resin in applications requiring large quantities of resin because of the availability and low cost of soybean hulls compared with the higher cost of purified cellulose.

The limiting value of 0.71 mmol g<sup>-1</sup> of cationic sites g<sup>-1</sup> of hulls requires further attention as we would like to extend anion adsorption capabilities beyond this level. Two approaches to the problem are possible. First, search for other agricultural by-products that may be more amenable to quaternization than soybean hulls. Second, evaluate other methods of quaternization that employ different quaternizing reagents. Research on both fronts is currently under way.

#### DISCLAIMER

Mention of names of companies or commercial products is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture over others not mentioned.

#### REFERENCES

- Wartelle LH and Marshall WE, Citric acid modified agricultural by-products as metal ion adsorbents. *Adv Environ Res* 4:1–7 (2000).
- Youssef BM, Adsorption of acid dyes by cellulose derivatives. *Am Dyestuff Rep* 82:30–33 (1993).
- Navarro RR, Katsuhiko S, Naoyuki F and Matsumura, M, Mercury removal from wastewater using porous cellulose carrier modified with polyethyleneimine. *Water Res* 30:2488–2494 (1996).
- Antal M, Ebringerova A and Simkovic I, New aspects in cationization of lignocellulose materials. I. Preparation of lignocellulosic materials containing quaternary ammonium groups. *J Appl Polym Sci* 29:637–642 (1984).
- Antal M, Ebringerova A and Simkovic I, New aspects in cationization of lignocellulose materials II. Distribution of functional groups in lignin, hemicellulose, and cellulose components. *J Appl Polym Sci* 29:643–650 (1984).
- Ebringerova A, Antal M and Simkovic I, New aspects in cationization of lignocellulose materials III. Influence of delignification on reactivity and extractability of TMAHP-hemicelluloses. *J Appl Polym Sci* 31:303–308 (1986).
- Antal M, Simkovic I and Ebringerova A, New aspects in cationization of lignocellulose materials IV. Modification of

- aspen wood meal with quaternary ammonium groups. *J Appl Polym Sci* **31**:621–625 (1986).
- 8 Simkovic I, Mlynar J, Alföldi J and Antal M, New aspects in cationization of lignocellulose materials VII. Modification of spruce wood meal with quaternary ammonium groups. *J Appl Polym Sci* **33**:2651–2656 (1987).
- 9 Simkovic I, Mlynar J, Alföldi J and Micko MM, New aspects in cationization of lignocellulose materials. XI. Modification of bagasse with quaternary ammonium groups. *Holzforschung* **44**:113–116 (1990).
- 10 Simkovic I, Mlynar J and Alföldi J, Modification of corn cob meal with quaternary ammonium groups. *Carbohydr Polym* **17**:285–288 (1992).
- 11 Laszlo JA, Preparing an ion exchange resin from sugarcane bagasse to remove reactive dye from wastewater. *Tex Chem Color* **28**:13–17 (1996).
- 12 Simkovic I, Alföldi J, Auxtova O, Liskova D and Lerouge P, Chemical modification and fractionation of pea stem polysaccharides. *Carbohydr Polym* **29**:51–56 (1996).
- 13 Baes AU, Okuda T, Nishijima W, Shoto E and Okada M, Adsorption and ion exchange of some groundwater anion contaminants in an amine modified coconut coir. *Water Sci Technol* **35**:89–95 (1997).
- 14 Simkovic I, Preparation of anion exchangers from beech sawdust and wheat straw. *Ind Crops Prod* **10**:167–173 (1999).
- 15 Orlando US, Baes AU, Nishijima W and Okada M, Preparation of agricultural residue anion exchangers and its nitrate maximum adsorption capacity. *Chemosphere* **48**:1041–1046 (2002).
- 16 Orlando US, Baes AU, Nishijima W and Okada M, A new procedure to produce lignocellulosic anion exchangers from agricultural waste materials. *Bioresource Technol* **83**:195–198 (2002).
- 17 Kinniburgh DG, General purpose adsorption isotherms. *Environ Sci Technol* **20**:895–904 (1986).
- 18 US EPA, Ground water and drinking water, current drinking water standards, EPA 816-F-02, July (2002).
- 19 Renn CE, *Investigating Water Problems*. LaMotte Co, Chestertown, MD (1970).